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Biochar Production by Microwave and Conventional Slow Pyrolysis – Comparison of Energy Properties

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Abstract

The energy efficiency of torrefaction of biomass to stabilised biochar was studied using conventional (slow) and microwave (low temperature) pyrolysis. Conventional pyrolysis is approximately twice as energy efficient as microwave pyrolysis, in terms of the energy required to process a unit of feedstock. However, this is more than compensated for by the high energy content of the condensable and gaseous co-products from microwave pyrolysis, as these can be utilised to generate the electricity required to drive the process. It is proposed that the most efficient method of stable biochar

production is combination conventional heating with “catalytic” amount of microwave irradiation.

1 Introduction

Growing biomass is an excellent method by which atmospheric carbon dioxide can be sequestered, minimising the effect of greenhouse gases on the Earth’s atmosphere (Schneider, 1989). Traditionally there are two options for utilising this biomass - mulching to enhance soils and burning to recover energy (Demirbas, 2001). However, neither of these methods offers a long-term storage solution for this trapped carbon. With low energy density, high water content, poor grindability, poor handling properties and high heterogeneity, the performance and value of biomass in energy applications such as direct combustion is poor. One potential improvement to biomass is through thermal treatment such as torrefaction or pyrolysis; Fig. 1 shows energy flows, products and their applications. Mass loss during pyrolysis corresponds to release of volatiles and gases from the pyrolysing solid, resulting in a more stable carbon-rich product (I - biochar) with higher energy content and altered physical properties. This occurs by predominately removing oxygen [Crombie et al.] as energy neutral H₂O and CO₂ (II - gas), and volatile compounds (at pyrolysis temperature) with lower oxygen content (e.g. CO, CH₄, aldehydes, organic acids, anhydrosugars, phenols and furans – III - Volatiles). The variation in mass and energy distribution between these three major products significantly depends on pyrolysis conditions (heating rate, maximum temperature, type of biomass).(Bridgwater *et al.*, 1999) Therefore, for an optimum biomass utilisation strategy, it is important to have complete information about mass and energy balance obtained for given pyrolysis conditions.

(INSERT Figure 1 HERE)

The biochar product has two potential applications – energy through co-firing with fossil fuels and long-term carbon sequestration/ soil improvement.

Conversion of biomass into biochar and subsequent co-firing offers an attractive alternative to direct burning and co-combustion of biomass which has been widely adopted across Europe. Most large scale power plants in the UK are adding typically up to 10% (thermal) of biomass to their normal coal blends (Backreedy *et al.*, 2005). Biochar combustion, offers the potential to reduce CO₂ emissions of power generation, by offsetting emissions from fossil fuels. To maximise the offsetting potential of biomass combustion/ co-combustion, it is necessary to utilise biomass in high efficiency boilers, which at the moment means co-firing with coal (although high efficiency boilers dedicated to biomass are starting to appear). Co-firing of biomass with coal presents numerous challenges due to the very different nature of these two materials, and therefore a lot of development has been done on pre-treatment processes that make different types of biomass more amenable to co-firing with coal.

Thermal treatment, i.e. torrefaction/ pyrolysis is one of these processes, and offers several advantages. However, as this process requires energy, a careful consideration is needed to assess its benefits, when compared to other potential uses of biomass.

The second alternative for use of thermally treated biomass (biochar) is for carbon sequestration. The carbon in biochar is chemically and biologically more stable than carbon in the plant residue from which it is made; biochar carbon has been known to remain in soil for thousands of years (Warnock *et al.*, 2007; Manya, 2012). It is for this reason that biochar offers a method of locking up carbon that may have otherwise been emitted to the atmosphere, and in many cases offers a more effective option for climate change mitigation than offsetting of fossil fuel emissions by biomass combustion (Woolf *et al.*, 2010).

Both approaches require significant capital and energy input and it is therefore critical to achieve the highest possible efficiency by selecting the right technology and process settings.

Multiple methods of pyrolysis exist, each with different characteristics both in terms of inputs, temperature of operation and products generated (Bridgeman *et al.*, 2008; Brown *et al.*, 2011; Rowbotham *et al.*, 2012). This paper will focus on the lower temperature techniques of conventional slow pyrolysis (CP) that is an established technology suitable for biochar production, and microwave (MW) pyrolysis. The latter is a newer technology offering several interesting features such as controllability, (Sun, 2006), (Yu *et al.*, 2007) potentially improved energy (Ludlow-Palafox & Chase, 2001; Gronnow *et al.*, 2005; Shankar *et al.*, 2009) and cost efficiency (Chemat *et al.*, 2006), which is now accessible at both pilot (Clark & Sutton, 1996) and industrial scale (Croda, 2012). Therefore this paper aims to determine the energy balance involved in conversion of biomass to biochar, using the two methods. This work focussed on the lower temperature range, as that is where MW pyrolysis appears to be most effective and offers potential advantages over CP (Mašek *et al.*, 2012). An estimation of biochar formation energy consumption has previously been published by Lehmann (Gaunt & Lehmann, 2008); this study focus only onto the conventional slow pyrolysis for agricultural wastes. A comparison of microwave and conventional pyrolysis has not been reported neither has wood chips as a feedstock.

2 Materials and methods

2.1 Materials

The raw materials used in our experiments were short rotation coppice willow wood chips (WC) supplied by Renewable Energy Suppliers Ltd (Koolfuel 15). The properties of the

feedstock are shown in Table 1. The feedstock was used as received, without any additional pre-processing.

(INSERT TABLE 1 HERE)

2.2 Experimental apparatus and procedure

2.2.1 Slow pyrolysis/ Torrefaction using conventional heating (micro-scale)

Conventional pyrolysis of 0.7 g of wood chips was performed using a Netzsch STA 409 at a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$, across the temperature range 200-400°C under flowing N_2 at 100 mL min^{-1} .

2.2.2 Slow pyrolysis/ Torrefaction using conventional heating (laboratory-scale)

The pyrolysis apparatus used, shown Fig. 2A, is a fixed-bed reactor comprising a quartz glass reactor tube (50mm i/d) with a sintered glass plate at the base. The reactor tube is heated by a 12kW infrared image furnace (ULVAC RHL-P610C) with temperature control based on a thermocouple immersed within the test sample. Inert gas (nitrogen) is supplied to the work-tube at a controlled rate and, after preheating in the bottom part of the reactor, it passes up through the sample carrying volatiles and syngas into a condenser train.

The condenser train consists of two parts; first the gas passes through a heated filter ($170\pm 15^{\circ}\text{C}$) where any entrained particulates are separated, as well as some heavy tars. Second, the particulate-free gas passes through an air condenser with ambient-temperature receiver and two cold traps maintained at -50 to -30°C using liquid nitrogen-cooled acetone. The composition of the non-condensable gases exiting the second trap is continuously monitored using an online quadrupole mass spectrometer (Hiden HPR-20 QIC, Hiden Analytical Ltd.). The gasses are collected in a series of gas bags (Cali-5-Bond™ and SKC

flex-foil) for offline analysis at the end of the run. A volumetric gas flow meter (Ritter, TG5) is then used to empty the gas bags and therefore determine the volume of gas produced during the experimental run. Differential pressure over the sample bed and gauge pressure at the reactor head are also monitored.

In a typical conventional slow pyrolysis (CP) experiment a biomass sample (approx. 50g) was charged to the reactor tube before assembling the apparatus. Pressure sensors were zeroed and the reactor was purged with nitrogen before establishing a steady flow rate of nitrogen as carrier gas; an inlet flow of 0.33 l min^{-1} was used giving a calculated linear cold flow velocity within the empty reactor tube of 3 mm s^{-1} .

(INSERT FIGURE 2 HERE)

The sample was heated at an average heating rate of $5 \text{ }^{\circ}\text{C min}^{-1}$ to the required hold temperature (200, 250, 300 and $350 \text{ }^{\circ}\text{C}$). The hold temperature was maintained for 10 minutes before the heating was stopped and the sample cooled under nitrogen (rapid cooling ensured by built in water cooling of the furnace).

Throughout each experiment, temperature within the sample bed, reactor pressure and differential pressure were monitored and logged. Product yields are given as recovered yields expressed as percent by weight of dry feed. Not all solid and liquid products could be recovered from the apparatus; handling losses were estimated at between 5-10% in total.

2.2.3 Microwave pyrolysis. (micro-scale)

Samples of wood chips (ca. 600 mg) were weighed out into a microwave tube (10 mL), and then sealed using the microwave tube lid. The sample was placed in a CEM Discover laboratory microwave (300 W Max. 2.45GHz monomode). The sample was irradiated under varying conditions, typically power: 300 W and temperature: $100\text{-}230^{\circ}\text{C}$. After microwave

treatment, the sample was removed from the microwave and washed with acetone to remove condensed volatile components. The mass of solid lost as a result of microwave treatment was carefully monitored.

2.2.4 Microwave pyrolysis. (laboratory-scale).

The microwave (MW) treatment of biomass was carried out using a Milestone ROTO SYNTH Rotative Solid Phase Microwave Reactor (Milestone Srl., Italy) fitted with a VAC 2000 vacuum module in series. Samples were exposed to a maximum microwave power of 1200W with an operating microwave frequency of 2.45 GHz (wavelength 12.2 cm, multimode). Samples of wood chips (ca. 130g) were placed in 2L glass flask within the microwave cavity (see Fig. 2B). Microwave pyrolysis was carried out under vacuum (initial pressure ca. 30 mbar) and constant microwave power (1200W). Biochar from wood was obtained at 170°C. During pyrolysis, biochar and a number of pyrolysis oil fractions were obtained. Temperature measurements were carried out using two different methods; temperature of the volatile fractions was measured using a thermocouple on the exit tube, and that of the solid fraction was measured via infrared detector within the cavity (See Fig. 2B). Sample temperatures of the solid and exited volatiles were found to be within 15 °C of each other, indicating that there was a good correlation of temperature measurement. This is further evidence for use of IR measurement as an accurate method to measure temperature within microwave biomass pyrolysis systems. Due to the instantaneous evaporation of the newly formed bio-oil, the heat of evaporation will retard overheating at pyrolysis centres, whilst the vapour will heat the bulk of the solid as it diffuses out from the pyrolysis centre (Budarin *et al.*, 2011). At temperatures below 70°C physisorbed water was collected; with increasing temperature chemisorbed water was observed around 110-120°C, and finally at temperatures between 130 and 160°C non-compressible gases and bio-oil were observed.

The process pressure was monitored at all times. Liquid fractions were collected via a water-cooled vacuum trap, which collected the condensed vapours produced during the process.

2.3 Characterisation of products

2.3.1 Elemental analysis

A known mass of sample is combusted within an Exeter CE440 Elemental Analyser in an oxygen atmosphere.

2.3.2 Heating value

A known mass of sample (approx. 1g) was combusted in an oxygen - enriched atmosphere within a Parr 6200 bomb calorimeter, and its calorific value (kJ g^{-1}) determined.

2.3.3 Carbon stability

The carbon contained in biochar can be classified into several fractions depending on its stability, i.e. recalcitrance to environmental degradation. The stable carbon fraction was determined for all biochars using an accelerated ageing assay (Cross & Sohi). This assay involved thermal and chemical oxidation of milled biochar samples. Accelerated ageing using oxidation was used given that degradation of biochar in soils is a typically oxidative process. Samples were placed in 5% hydrogen peroxide and heated to 80 °C, and carbon stability then was calculated gravimetrically using the %C data of samples before and after oxidation.

3 Results and discussion

3.1 Product yields

Fig. 3 shows the solid mass retained for CP and MW pyrolysed wood chips prepared over a range of pyrolysis temperatures. As can be seen, the thermal behaviour of wood chips is dramatically different for the two methods; under conventional heating conditions the major mass loss is observed at temperatures of around 250°C, whereas under microwave heating

conditions the major mass loss occurs at around 160°C. Additionally there is a considerable difference in the temperature range over which the major share of decomposition occurs: 130°C for CP and 50°C for MW pyrolysis.

(INSERT FIGURE 3 HERE)

As illustrated in Table 2 at a temperature relating to the end of this major mass loss process (350 °C and 170°C for CP and MW respectively), the two methods of pyrolysis (CP and MW) both show differences in the distribution of products. MW pyrolysis preferentially generates liquids and gases, yielding 27.3 wt% biochar from the wood chips whereas CP yields predominantly solid products (39.8%). Biochar yield from both microwave and conventional pyrolysis at this point (end of this mass loss peaks) has been observed to be largely independent of scale, in the range investigated (see Fig. 3).

(INSERT TABLE 2 HERE)

3.1.1 Carbon content, yield and stability

For long-term carbon storage, high carbon stability is required with ideally with minimal oxygen content, hence stable carbon content and yield of the final biochar are of crucial importance for carbon sequestration. Table 3 shows the carbon content, char yield and carbon stability of biochar produced by the two heating methods at temperatures corresponding to the end of their respective mass loss peak.

(INSERT TABLE 3 HERE)

It can be seen that MW biochars show comparable stability to CP chars obtained at higher temperatures (350°C). This is most likely due to the same degree of conversion being achieved by the two methods, despite the considerably lower temperature for MW heating, as evidenced by other data (Mašek *et al.*, 2012). Nevertheless, due to the low carbon yields of

MW biochar the overall yields of stable carbon are low (around 21-25 %C) when compared to CP chars (around 35%C). This means that although MW pyrolysis conducted at very low temperatures (170-200 °C) produces chars with stability considerably higher than that of the starting material or even materials produced by CP at comparable temperatures, the overall carbon sequestration potential of this technology is limited by the low yield of stable carbon.

3.1.2 High Heating Value (HHV)

Fig. 4 shows the significant difference in high heating value (HHV) of biochar samples prepared from wood chips using CP and MW pyrolysis.

(INSERT FIGURE 4 HERE)

It can be seen from Fig. 4 that biochar with same HHV value can be obtained at temperatures around 150°C lower using microwaves compared to conventional pyrolysis. In the case of MW pyrolysis, a significant increase in calorific value occurs even at 150°C, whereas for CP comparable increase occurs only at around 300°C. The difference in temperature of the activation stage of these two types of pyrolysis methods, using the example shown for wood chips, is significantly higher than the difference found for activation of the individual compounds cellulose and hemicelluloses (Budarin *et al.*, 2010). Further evidence of this can be seen in the comparison of microwave influence on biochar HHV produced from the major biomass structural components and wood chips (Fig. 5).

(INSERT FIGURE 5 HERE)

The overall trend with the model biomass compounds when heated via conventional or by microwave is that hemicellulose is activated before cellulose, with those treated with microwaves being activated first. The gradients for the entire microwave heated samples and

the conventional heated cellulose are similar, leading to the possibility that the decomposition pathways i.e. the loss of H₂O, CO or CO₂ etc. are the same.

The microwave treated wood sample is activated at lower temperature despite being composed mainly of the model compounds hemicellulose and cellulose, and the less microwave active species lignin. This suggests that this type of wood contains a highly microwave active species, such as resin or primary oils, which are not as active under conventional heating as under MW heating.

3.1.3 Calculated energy input required for solid fuel production.

Energy characteristic of wood components and products obtained during pyrolysis combined with mass balance of the process are summarised in Table 4.

(INSERT TABLE 4 HERE)

Based on data shown in Table 3, the energy required for microwave assisted pyrolysis of 1 ton of wood was calculated (see Fig. 6).

(INSERT FIGURE 6 HERE)

To a first approximation, the electrical energy which is required for microwave pyrolysis of wood was estimated at approximately 1080 MJ/ton based on data shown in Fig. 6. However, if conversion of heat energy to electrical power (with average efficiency 38%) is taken into account (CHP.Focus, 2012), the overall energy requirement for microwave assisted pyrolysis of wood to a stable carbon becomes 3000 MJ/ton (3.0 kJ/g).

(INSERT FIGURE 7 HERE)

The energy input required for conventional pyrolysis of one ton of wood chips was calculated to be 1173 MJ/ton (Fig. 7). Taking into account the fact that conventional heating does not

necessarily require conversion of heat to electricity this value, which corresponds to approximately 6% of the CV of original feedstock, is lower than total energy estimated for microwave pyrolysis of wood chips (3000 MJ/ton – Fig. 6), i.e. 17% of feedstock CV. Consequently, the energy required to produce one ton of biochar from conventional pyrolysis (2940 MJ/ton) is approximately one third that for MW pyrolysis (11720 MJ/ton). However, combination heating using conventional pre-heating to near pyrolysis temperatures (160-180°C), followed by microwave activation of the biomass through the pyrolysis temperature, utilising the high energy input and heating rates which microwaves can achieve could significantly reduce the time needed to process the material and operating temperature whilst maintaining the energy advantage of conventional heating. This study does not take into account potential of exothermic processes which may occur and influence the overall energy efficiency for a process.

3.1.4 Energy of Solid and Volatile fractions.

The majority of components in the evolved gases are combustible and therefore energy from the feedstock contained in these co-products can be potentially recovered using either established internal/ external combustion engine technologies for electrical power generation or simply used for direct heating of a CP or other process by combusting the gaseous and volatile products. Recovery and integration of this energy stream would be hugely beneficial to the economics and practicality of a torrefaction/ pyrolysis process. Fig. 8 shows the energy released during the conversion process (black bar) calculated based on data shown in Fig. 3 and 4 versus the energy input required to operate the process at the relevant temperatures (cross-hatch bar). As can be seen for MW pyrolysis there is a clear optimum point around 170°C where there is a trade-off between process energy input, energy release and product energy content.

(INSERT FIGURE 8 HERE)

The goal of this operation is to stabilise carbon through removal of oxygen (Crombie *et al.*, 2012), while maximising positive co-benefits of biochar (e.g. agricultural), with the minimum energy input. Hydrogen is crucial in this step as transfer of hydrogen to bio-oil/gas increases the energy output whereas, conversion to CO₂ offers no benefits in terms of recoverable energy.

Comparison of energy input and output for production of one kilogram of biochar by both processing methods are shown in Fig. 9. These demonstrate the relatively low energy requirement to drive the pyrolysis process in contrast to the high levels of energy released as bio-oil and gas. As discussed, the CP process uses half the energy required by MW pyrolysis, however the energy of the volatiles released during MW pyrolysis is approximately double that for CP. These results show that pyrolysis processes, by either technology, have potential to be self-sufficient in process energy demand with significant excess energy available for other uses.

(INSERT FIGURE 9 HERE)

4 Conclusions

This work has provided some new insights into the differences between biochar produced by low temperature microwave pyrolysis (MW) and that of conventional pyrolysis (CP). The process energy, energy of volatiles and char, carbon in char and stability of char were compared and contrasted.

It has been observed that both CP and MW pyrolysis systems can produce a long term stabilised form of carbon that may be suitable for soil improvement and carbon sequestration. Review of the process, indicates the CP is approximately twice as energy efficient as MW pyrolysis. However, when extending the system to a simple biorefinery, the manner in which energy is recovered from the evolved volatile compounds and the total process energy for CP and MW pyrolysis becomes energy generating. In this approach, microwave-assisted pyrolysis has advantage over conventional pyrolysis as the process occurs at lower temperatures and more energy is released.

To extend this initial comparison, further studies of interest include:

- i) Investigation of a combined conventional and microwave pyrolysis systems, utilising the enhanced microwave activation effect at the pyrolysis onset temperature.
- ii) Determination of the optimum heating rate required for pyrolysis – microwave heating has highly tuneable heating rates and this is yet to be used in biochar production.
- iii) An LCA study would be needed to compare fully the two technologies as the different carbon sequestration potential is likely to be offset by the potential for the renewable energy and materials co-products.

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Table 1. Elemental and structural composition of Willow chips.

	C	H	N	ash	moisture	cellulose	hemicellulose	lignin	CV
feedstock	[wt. %] a	[wt. %] a	[wt. %] a	[wt. %] b	[wt. %] b	[wt. %] b	[wt. %] b	[wt. %] b	[MJ/kg] a
Willow chips (WC)	48.29	6.01	1.04	0.80	9.10	37.20	36.00	18.70	19.78
(a) - on dry basis			(b) - on as received basis						

Table 2. Wood chips pyrolysis product distribution (Laboratory scale).

Pyrolysis type	Temperature °C	Char %	Liquid %	Gas %
MW	170	27.3	42.2	30.5
Conventional	350	39.8	39.9	20.2

Table 3. Char yield, carbon content, stability and stable carbon yield obtained for dry wood.

Sample	T, °C	C, wt% ^a	Char yield wt%	C yield wt% C-basis ^b	Carbon stability wt% char-C ^c	Stable carbon yield, wt% c- basis ^d
Conventional	350	70.7	39.8	58.2	60.5	35.3
Microwave	170	65.2	27.3	36.9	58.0	21.4

^a Carbon content of biochar. ^b yield of carbon in biochar as fraction of carbon in feedstock ^c fraction of carbon retained after oxidative treatment ^d yield of stable carbon as a fraction of carbon in feedstock .

Table 4. Energy and mass characteristics for slow and microwave pyrolysis of wood in laboratory scale system

Wood chips components and products		Contents (%)	Heat capacity (kJ/kg*K)	Gas phase Heat capacity (kJ/kg*K)	Vaporisation energy (kJ/kg)
Structural components	Physisorbed water	11	4.2	2.08	2260
	Dry wood	89	1.59 ^a	-	
Pyrolysis water	MW (170°C)	23.8	4.2	2.08	2260
	CP (350°C)	18.4			
Bio-Oil	MW(170°C)	16.6	-	1.39 ^c	141 ^d
	CP(350°C)	17.9			
Biochar	MW(170°C)	25.6	1.2 ^b	-	-
	CP(350°C)	39.8			
^a (Ragland <i>et al.</i> , 1991)					
^b C _p = 1003.2+2.09(T-273) (Babu & Chaurasia, 2004)					
^c (Johari <i>et al.</i> , 2011)					
^d (Suuberg & Oja, 1997)					

Figure legends

Fig. 1. Potential products of biomass pyrolysis and their potential utilisation.

Fig. 2. Schematics of Experimental Equipment: A – Conventional Slow Pyrolysis (Pilot Scale) and B – Microwave-assisted Pyrolysis (Laboratory Kilo Scale).

Fig. 3. Comparison of char yield obtained by A) MW and B) CP pyrolysis.

Fig. 4. Influence of pyrolysis temperature on calorific value of biochar produced using CP (solid spheres) and MW pyrolysis (half spheres).

Fig. 5. Comparison normalised improvements of char obtained from hemicellulose, cellulose and wood obtained with CP and MW methods.

Fig. 6. Estimation of energy efficiency of microwave pyrolysis.

Fig. 7. Estimation of energy efficiency of conventional pyrolysis.

Fig. 8 Comparison energy balance for A) CP and B) MW pyrolysis of wood chips.

Fig. 9. Comparison of Energy balance of process of production 1kg of biochar by CP and MW pyrolysis. Process energy is energy spent for pyrolysis. Volatiles energy is energy of volatiles. Produced bio-energy is a difference between energy of volatiles and process energy.